

Neutralization Potential Determination of Siderite (FeCO₃) Using Selected Oxidants

E. B. Haney, R. L. Haney, L. R. Hossner, and G. N. White*

ABSTRACT

Siderite (FeCO₃) is commonly found in coal overburden and, when present, can cause interference in the determination of neutralization potential (NP). Under acidic testing conditions, FeCO₃ reacts to neutralize acid, which contributes to the NP. However, continued weathering of FeCO₃ (oxidation of Fe²⁺ and hydrolysis of Fe³⁺) produces a neutral to slightly acidic solution. The effects of hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), and O₂ on the laboratory measurement of NP of siderite samples taken from overburden were examined. All oxidation treatments lowered the NP values of the siderite samples as compared with the standard USEPA method. However, oxidation with H₂O₂ produced variable results depending on the amount of H₂O₂ added. Neutralization potential values obtained after oxidation treatments were highly correlated with Mn concentration. Reaction products (i.e., 2-line ferrihydrite) of siderite samples with H₂O₂ and KMnO₄ were not representative of natural siderite weathering. Oxidation with O₂ produced the lowest NP values for siderite samples. The reaction products produced by oxidation with O₂ most closely represent those intermediate products formed when siderite is exposed to atmospheric weathering conditions. Oxidation with O₂ also proved to be the most reproducible method for accurately assessing NP when siderite is present in overburden samples.

PRESENT reclamation procedures in Texas allow for the use of mixed overburden as a topsoil substitute. Selectively handled overburden may be used to replace topsoil if it is of equal or better quality than the original topsoil and is the best available material to support revegetation. Determination of a suitable topsoil substitute is based on chemical and physical analyses of the overburden and undisturbed topsoil. The analyses include, but are not limited to, pH, net acidity, net alkalinity, nutrient status, particle size analysis, and texture class (Railroad Commission of Texas, 1998). Care must be taken to prevent acid soils and/or acid drainage due to the oxidation of acid-forming materials (AFM) that are commonly found in reduced overburden and in association with lignite seams. To assess residual soil acidity and the potential of acid drainage, the acid-base account (ABA) for overburden samples is commonly determined using Eq. [1] or Eq. [2] where NP is the neutralization potential, PA is the potential acidity, and EA is the exchangeable acidity.

$$ABA = NP - (PA + EA) \quad [1]$$

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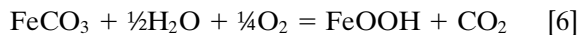
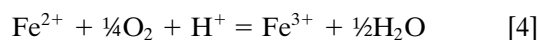
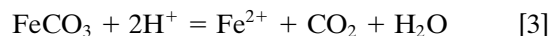
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$$ABA = NP - PA \quad [2]$$

When the ABA is positive, one assumes there is an adequate amount of NP to neutralize any acidity present in the mine-soil. If the ABA is negative, the overburden may produce acid mine soils and/or acid drainage and should be buried more than 1.2 m (4 feet) below the surface.

Neutralization potential measures easily weatherable minerals (i.e., olivine and micas), including carbonates, present in an overburden (Doolittle et al., 1992). The NP of an overburden is determined using USEPA Method 600/2-78-054 3.2.3 (Sobek et al., 1978). The sample is first given a fizz rating (none, slight, moderate, or severe) based on visual and audible ratings after treating the sample with 1:3 HCl. Samples are then treated with a known amount of HCl, determined by the fizz rating, and heated until the reaction is complete (sample settles on bottom of flask). The excess acid is titrated with NaOH to a pH of 7.0. Neutralization potential is reported in terms of calcium carbonate (CaCO₃) equivalent and is calculated directly from the amount of acid consumed by the sample.

Siderite (FeCO₃) is frequently present in anoxic overburden and can cause false positive or unrealistically high NP values. Siderite is susceptible to oxidation when exposed to atmospheric weathering conditions, which can be described by Eq. [3] to [6] (Frisbee and Hossner, 1995; Lindsay, 1979).

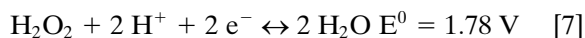


Continued weathering of FeCO₃ produces a neutral reaction when lepidocrocite (γ-FeOOH) or goethite (α-FeOOH) is the reaction product. Atmospheric weathering conditions favor alteration of siderite to goethite through dissolution and ensuing oxidation or precipitation (Senkayi et al., 1986). However, under acidic testing conditions, FeCO₃ reacts to neutralize acid, which contributes to the NP (Eq. [3]). Siderite affects NP because Fe²⁺ released during acid digestion does not undergo complete oxidation and hydrolysis (Eq. [4] and [5]) during NP evaluation (Doolittle et al., 1992; O'Shay et al., 1990).

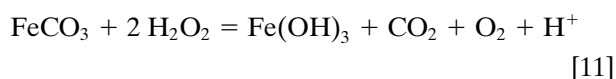
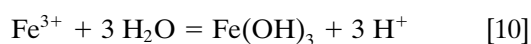
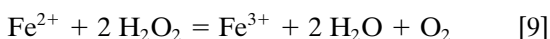
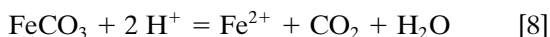
Alterations to the USEPA method are needed to accurately assess the NP of overburdens containing

Abbreviations: AAS, atomic adsorption spectroscopy; ABA, acid-base account; AFM, acid-forming materials; EA, exchangeable acidity; GR1(CO₃), green rust; NP, neutralization potential; PA, potential acidity; XRD, X-ray diffraction analysis.

siderite. Skousen et al. (1997) studied the effects of H_2O_2 on NP values for overburden soils from Pennsylvania and West Virginia. Hydrogen peroxide is an effective oxidizing agent at pH values below 5.8 as shown in Eq. [6] (Diehl, 1970).



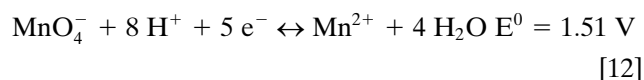
Hydrogen peroxide serves to oxidize Fe^{2+} after samples are digested with HCl during NP testing. Hydrogen peroxide theoretically acts to oxidize Fe^{2+} to Fe^{3+} , which is subsequently hydrolyzed to an iron hydroxide ($\text{Fe}(\text{OH})_3$) as shown in Eq. [8–11] (Lindsay, 1979; Schwertmann and Cornell, 1991).



The overall reaction (Eq. [11]) shows that, with $\text{Fe}(\text{OH})_3$ as the reaction product, 1 mol of FeCO_3 consumes 1 mole of H^+ on dissolution, oxidation, and hydrolysis versus 2 mol H^+ consumed by nonoxidized samples. Therefore, NP values of oxidized samples should decrease accordingly. Skousen et al. (1997) found that H_2O_2 decreased NP values of samples containing siderite due to complete oxidation of Fe^{2+} and hydrolysis of Fe^{3+} .

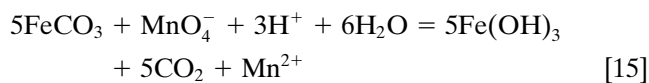
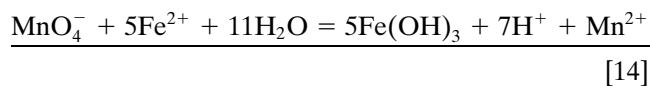
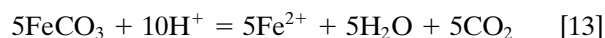
Analytical laboratories commonly use H_2O_2 for determining NP when siderite is assumed to be present in overburden samples. First, samples are analyzed according to the USEPA method. After titration to pH 7.0, samples are treated with 5 mL of 30% H_2O_2 , and then titrated again to pH 7.0. Neutralization potential values are calculated from the total amount of NaOH needed during the first and second titrations.

Potassium permanganate is a strong oxidizing agent (Eq. [12]) that serves as its own color indicator during oxidation–reduction titrations (Diehl, 1970).



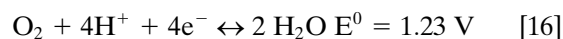
The MnO_4^- ion is intensely purple, and the Mn^{2+} ion is colorless. As long as some reducing agent is being titrated, the solution is colorless, since the purple MnO_4^- ion being added is converted to Mn^{2+} . However, when the reducing agent has been consumed, the next drop of titrant will turn the solution light purple or pink. Therefore, the end point occurs one drop beyond the stoichiometric point when all of the reducing agent has been consumed (Zumdahl, 1989).

The expected reactions of KMnO_4 with FeCO_3 are as follows:



Equation [15] indicates that 0.6 mol of H^+ are consumed for every mole of FeCO_3 oxidized and hydrolyzed. Oxidation is expected to decrease NP values by reducing the amount of acidity consumed by FeCO_3 from 2 H^+ to 0.6 H^+ mol^{-1} .

Oxygen is an effective natural oxidant. The standard reduction potential of O_2 is shown in Eq. [8] (Zumdahl, 1989).



Pure O_2 can be bubbled through the sample solution to provide the O_2 for Fe^{2+} oxidation. The reactions for the dissolution and oxidation of FeCO_3 under NP testing conditions using O_2 as an oxidant should be identical to natural weathering conditions (Eq. [3]–[6]).

The objective of this research was to examine the effects of the oxidants; H_2O_2 , KMnO_4 , and O_2 on the reaction of siderite during NP determination and to study the resulting NP values. These experiments were designed to evaluate potential methods for NP determination in overburden samples containing siderite.

MATERIALS AND METHODS

Sample Analysis

Two siderite samples (A and B) were collected from lignite mine overburdens, crushed, and ground in an agate mortar to pass a 250- μm (60-mesh) sieve. The mineral composition of the siderite samples was determined using X-ray diffraction analysis (XRD). X-ray diffraction analysis was also performed on reagent-grade MnCO_3 and FeCO_3 reference samples. Minerals were identified from XRD patterns. Inorganic C was determined using the simple titrimetric method by Bundy and Bremner (1972). The method was altered to allow samples to digest in 2.0 M HCl for 2 d to ensure complete dissolution of minerals. Iron, Ca, Mn, and Mg concentrations of subsamples were determined using atomic adsorption spectroscopy (AAS) after samples were digested with 2.0 M HCl and filtered. The cation concentrations were used to calculate theoretical NP values using stoichiometric relationships for the dissolution of FeCO_3 , CaCO_3 , MgCO_3 , and MnCO_3 under NP testing conditions. For example, Eq. [8] to [11] as described above were utilized to calculate the theoretical NP of 2 g of FeCO_3 after acid dissolution and oxidation with H_2O_2 . The theoretical NP value was directly calculated from the theoretical amount of NaOH needed to neutralize the amount of acid produced during the reaction of FeCO_3 with HCl and H_2O_2 .

Neutralization Potential Determination

Subsamples of the siderite samples were weighed into flasks to contain 0.05, 0.10, and 0.20 g of siderite sample (equal to 2.5, 5.0, and 10.0% of a 2-g sample). Neutralization potential was determined on siderite subsamples and reagent-grade MnCO_3 , FeCO_3 , and CaCO_3 using USEPA Method 600/2-78-054 3.2.3 (Sobek et al., 1978).

All samples were digested with 20 mL of 0.1 M HCl (because of the “none” fizz rating) and heated until reaction was complete (sample residue settled on bottom of flask). Samples were brought to 125 mL volume with deionized water, then boiled for 1 min. Samples were allowed to cool to room temperature ($\sim 25^\circ\text{C}$), then titrated to pH 7.0 with ~ 0.1 M NaOH

Table 1. Summary of methods used to determine neutralization potential in samples of siderite (FeCO_3).

USEPA Method 600/2-78-054 3.2.3†	Oxidant		
	Hydrogen peroxide (H_2O_2)‡	Potassium permanganate (KMnO_4)	O_2
Add 1 or 2 drops of 1:3 HCl to sample and rate the "fizz" as none, slight, moderate, or severe Weigh 2 g of <60 mesh sample into flask Add HCl according to fizz rating Heat until reaction complete Add DI water to 125 mL Boil contents for 1 minute Cool to room temperature Titrate to pH 7 with NaOH Determine control value using same method	N/A weigh 2 g of <60 mesh sample into flask add 20 mL 0.1 M HCl heat until reaction complete add DI water to 125 mL boil contents for 1 min cool to room temperature filter half of set of samples add 5 or 10 mL H_2O_2 boil for 5 min cool to room temperature titrate to pH 7 with NaOH determine control value using same method	N/A weigh 2 g of <60 mesh sample into flask add 20 mL 0.1 M HCl heat until reaction complete add DI water to 125 mL boil contents for 1 min cool to room temperature titrate with 0.1 M KMnO_4 until pink color forms titrate to pH 7 with NaOH determine control value using same method	N/A weigh 2 g of <60 mesh sample into flask add 20 mL 0.1 M HCl heat until reaction complete add DI water to 125 mL boil contents for 1 min cool to room temperature insert aerator attached to air or O_2 tank into flask titrate to pH 7 with NaOH determine control value using same method

† Method of Sobek et al. (1978).

‡ Method of Skousen et al. (1997).

using a pH meter and combination electrode. Neutralization potential was reported in grams CaCO_3 equivalent kg^{-1} substrate and was determined directly from the amount of excess acid titrated. Solution color (precipitate formed) was determined before and during titration with NaOH using the Munsell Soil Color Charts. Precipitates formed during titration were filtered, dried, and analyzed using XRD spectroscopy.

Neutralization potential was also determined on siderite subsamples and reagent-grade MnCO_3 , FeCO_3 , and CaCO_3 following digestion in acid and oxidation of Fe^{2+} with H_2O_2 , KMnO_4 , and O_2 . Alterations to the USEPA method are listed in Table 1. Hydrogen peroxide, KMnO_4 , or O_2 were incorporated as oxidants and summarized as follows.

Hydrogen Peroxide

Samples digested in 0.1 M HCl according to the USEPA method were cooled to room temperature and gravity filtered through Whatman 42 filter paper. The filtered solution was then treated with 5 mL of 30% H_2O_2 and boiled for 5 min. Samples were hand titrated to a pH of 7.0 using 0.1 M NaOH. The method was repeated using 10 mL of 30% H_2O_2 and again on subsamples that were not filtered after acid digestion. Solution color (precipitate formed) was determined before and during titration with NaOH using the Munsell Soil Color Charts. Precipitates formed during titration were filtered, dried, and analyzed using XRD spectroscopy.

Potassium Permanganate

Samples digested in 0.1 M HCl were cooled to room temperature and treated with 1.0 M KMnO_4 (pH 7). Potassium permanganate was slowly added to the samples until a pink color formed, indicating an excess of oxidant and complete oxidation of Fe^{2+} . Samples were then titrated with 0.1 M NaOH to pH 7.0. Precipitate color was not determined during titration due to dominance of pink color from KMnO_4 .

Oxygen

Samples digested in 0.1 M HCl were treated with pure O_2 . The flask containing the digested sample was equipped with a small fish-tank aerator that was attached to a tank of O_2 . Gas was vigorously bubbled through the sample solution while titrating to pH 7.0 with 0.1 M NaOH. Oxygen was bubbled through the sample for the duration of the titration. The length of time that the solution was in contact with the O_2 varied

depending on the amount of acidity consumed during digestion (i.e., the mineralogy of the sample). Solution color (precipitate formed) was determined before and during titration with NaOH using the Munsell Soil Color Charts. Precipitates formed during titration were filtered, dried, and analyzed using XRD spectroscopy.

Statistical analysis was performed using one-way ANOVA (SPSS, 1997).

RESULTS AND DISCUSSION

Sample Identification

X-ray diffraction results combined with Fe, Mn, Ca, and Mg analysis indicate that Sample A is composed largely of siderite (with Fe partially substituted by Mn, Ca, and Mg) and quartz. Samples A and B have enough Mn substitution to be classified as manganoan siderite and also contain quartz (Fig. 1). Peaks located around $26.6^\circ 2\theta$ are characteristic of quartz. Peaks around $32^\circ 2\theta$ are indicative of siderite. A peak at approximately $31.5^\circ 2\theta$ indicates the presence of manganoan siderite in Samples A and B. The dominant peak that is character-

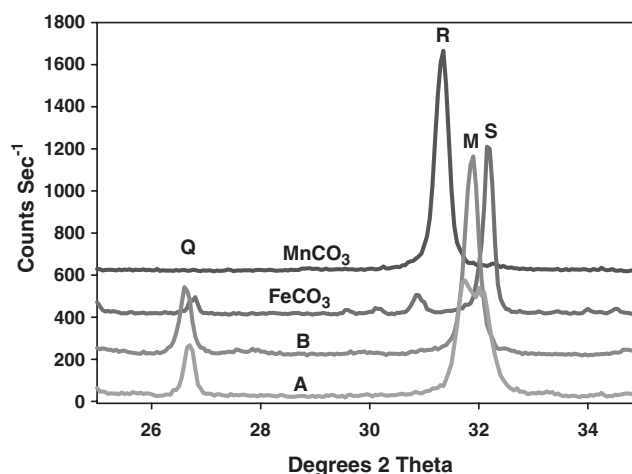


Fig. 1. X-ray diffractograms showing major peaks for Samples A and B as compared with reagent-grade rhodochrosite (MnCO_3) and siderite (FeCO_3). S = siderite, M = manganoan siderite, R = rhodochrosite, and Q = quartz.

Table 2. Properties of siderite samples A and B.

Sample	CO ₃ ²⁻	Ca	Mg	Fe	Mn	CO ₃ ²⁻	Ca	Mg	Fe	Mn
	g kg ⁻¹					cmol _c kg ⁻¹				
Siderite A	360.0	58.7	13.1	248.1	5.9	1200	300	110	880	20
Siderite B	338.0	41.2	19.7	218.0	37.6	1130	200	170	780	140

istic of FeCO₃ is shifted to the left of the dominant peak for reagent-grade FeCO₃ toward the MnCO₃ peak, suggesting Mn substitution.

Total Fe, Mn, Ca, and Mg (cmol_c kg⁻¹) for siderite Samples A and B, 1310 and 1290, respectively, should be equal to the CO₃²⁻ present (1200 and 1130, respectively) (Table 2). Data on elemental composition show that there is a greater proportion of cations to CO₃²⁻, which may be due to the presence of mineral impurities. The Fe/CO₃²⁻ molar ratio in reagent-grade FeCO₃ is 0.93. The Fe/CO₃²⁻ ratio for Samples A and B (0.68 and 0.64) are <0.93, suggesting cation substitutions in the FeCO₃ lattice.

Neutralization Potential

Data in Fig. 3A show that 88% of the variability in USEPA procedure measured NP ($r^2 = 0.88$) can be attributed to the CO₃²⁻ content of the samples. Iron and Ca were strongly correlated to NP values, with r^2 values of 0.93 and 0.97, respectively. Magnesium and Mn substituted in the FeCO₃ lattice were not highly correlated to NP values obtained ($r^2 = 0.48$ and 0.04, correspondingly).

Siderite dissolves under acidic NP testing conditions to release Fe²⁺, which may oxidize to metastable intermediate products. When the Fe²⁺ liberated is titrated with NaOH during NP testing using the USEPA method, a green precipitate (5Y 4/2 olive gray to 5Y 2/1 black) is formed. The green color is characteristic of green rust [GR1(CO₃)], a ferrous-ferri hydroxy carbonate having the proposed chemical formula [Fe²⁺₄Fe³⁺₂(OH)₁₂][CO₃·H₂O] (Legrand et al., 2000). Green rust may form from partial oxidation of Fe(OH)₂ by dissolved O₂. The formation of the green color associated with GR1(CO₃) began around pH 2.5 and increased in intensity as pH increased, which is consistent with literature reviewed concerning formation of GR1(CO₃) from Fe(OH)₂ (Legrand et al., 2000). The green color of the precipitate changes to a reddish-gray color if filtered and air-dried. Green rust is a partially oxidized species and its precipitation during NP analysis supports the theory that FeCO₃ increases NP values because of incomplete oxidation and hydrolysis of dissolved Fe.

Neutralization potential values of 0.1 g of reagent-grade CaCO₃ were significantly higher than NP values of 0.1 g FeCO₃ and 0.1 g MnCO₃ (Fig. 2). Rhodochrosite (MnCO₃) NP values were 60% of CaCO₃-NP values, while FeCO₃-NP values were only 20% of CaCO₃-NP values.

Oxidation and Neutralization Potential

Hydrogen Peroxide

Since analytical laboratories do not filter their samples before treatment with H₂O₂, the nonfiltered, 5 mL

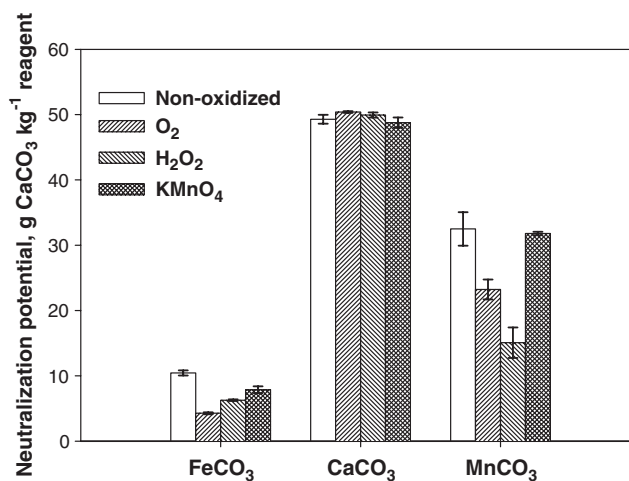


Fig. 2. Neutralization potential values for 0.1 g of reagent-grade CaCO₃, MnCO₃, and FeCO₃. Error bars indicate 1 SD.

treatment was used for the comparisons in Fig. 3B and 4. Data in Fig. 3B indicates that experimental NP values for the H₂O₂ treatment were highly correlated with Mn and Mg content ($r^2 = 0.81$ and 0.96, respectively). Sixty-five percent of the variability in NP values was due to CO₃²⁻ content. Neutralization potential values of siderite samples after oxidation were not highly related to Fe or Ca concentrations. Since the NP values after oxidation with H₂O₂ were not correlated to Fe concentration, we may infer that treatment with H₂O₂ decreased the effect of FeCO₃ on NP values. The data indicate that the dissolution of Mn and Mg carbonates is responsible for the NP values after oxidation with H₂O₂.

The data in Fig. 4 signify that NP values significantly decreased after oxidation with H₂O₂. The NP values varied between filtered and nonfiltered treatments (Fig. 5). The decreases in NP after oxidation as compared to the USEPA method were highly correlated with Ca, Mg, Fe, and Mn concentration for all treatments. Nonfiltered treatments produced lower NP values than filtered treatments, which may be due to oxidation of solid siderite not dissolved during digestion. Neutralization potential values were not consistently lower or higher between 5 and 10 mL H₂O₂ treatments.

Experimental NP values of samples containing 2.5, 5, and 10% siderite with known cation concentrations were compared with theoretical NP values based on stoichiometric equations for: (i) the dissolution of MnCO₃, MgCO₃, and CaCO₃; and (ii) the dissolution, oxidation, and hydrolysis of FeCO₃. Experimental NP values were less than the theoretical NP values based on carbonate dissolution, indicating that the siderite may not be completely dissolving in the acid solution. Data presented in Fig. 6 show that the NP values obtained after all H₂O₂ treatments were highly correlated with theoretical NP values from dissolution of MgCO₃ and MnCO₃ in HCl (without oxidation and hydrolysis of Mn). Based on correlation values, NP values obtained using the 10 mL treatment correlated with theoretical MnCO₃ dissolution more so than NP values obtained using the 5 mL treatment. The NP values obtained from the nonfiltered treatments are more strongly correlated with theoretical

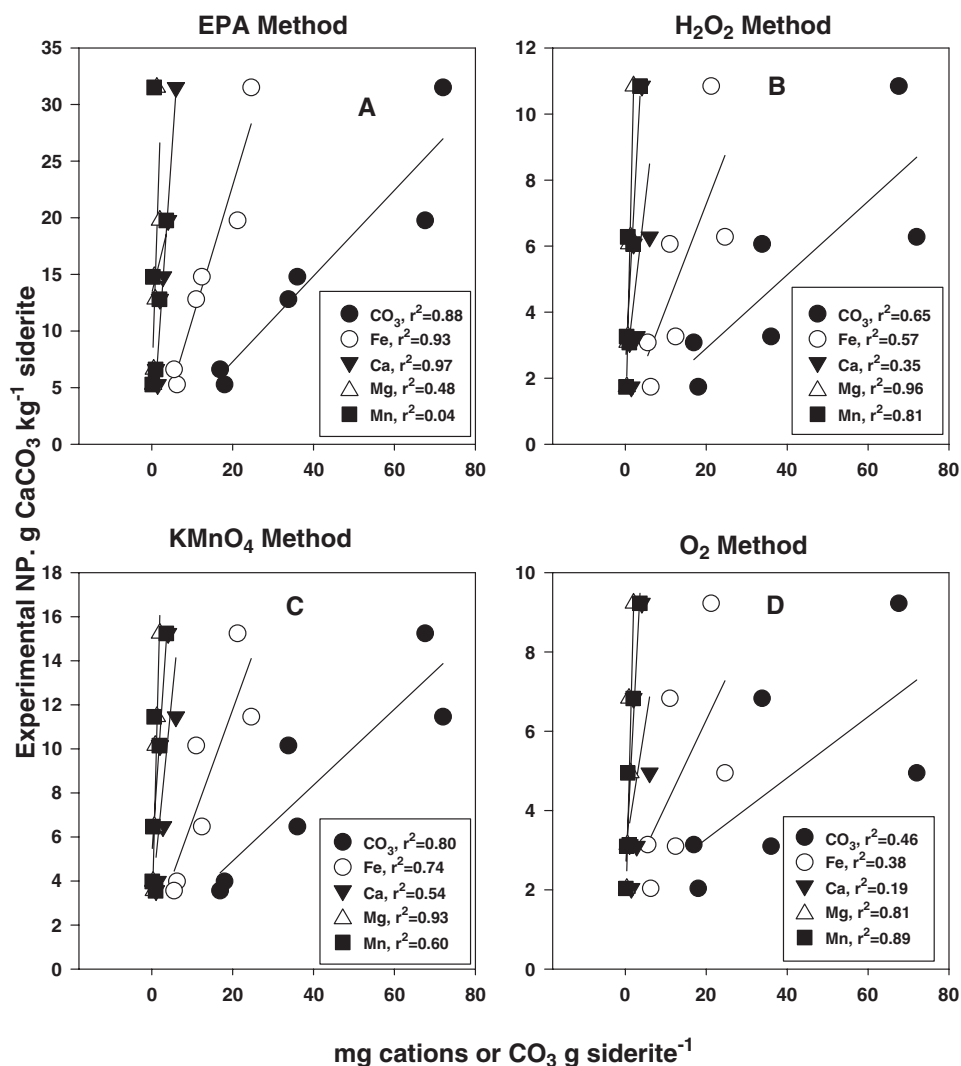


Fig. 3. Experimental neutralization potential (NP) values of siderite samples determined using USEPA Method 600/2-78-054 3.2.3 (Sobek et al., 1978) and oxidation treatments as compared with carbonate and cation concentrations.

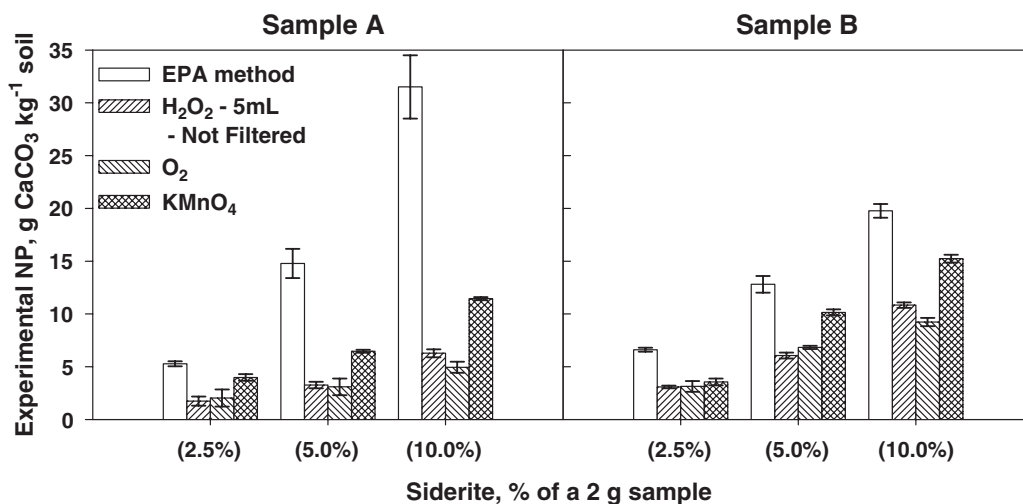


Fig. 4. Comparison of neutralization potential (NP) values obtained using USEPA Method 600/2-78-054 3.2.3 (Sobek et al., 1978) as compared with oxidation treatments. Error bars indicate 1 SD.

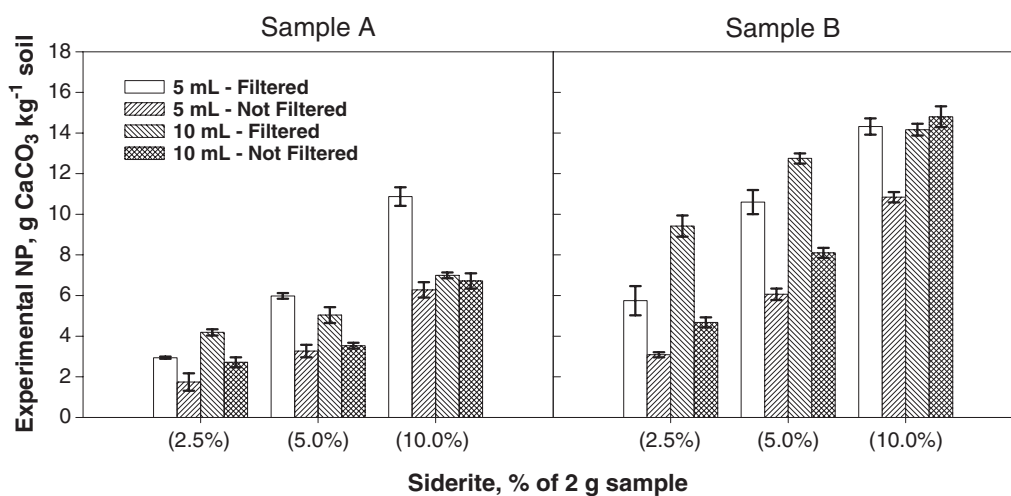


Fig. 5. Neutralization potential (NP) values of siderite samples determined using 5 or 10 mL of H₂O₂ on filtered and nonfiltered samples after digestion with 0.1 M HCl. Error bars indicate 1 SD.

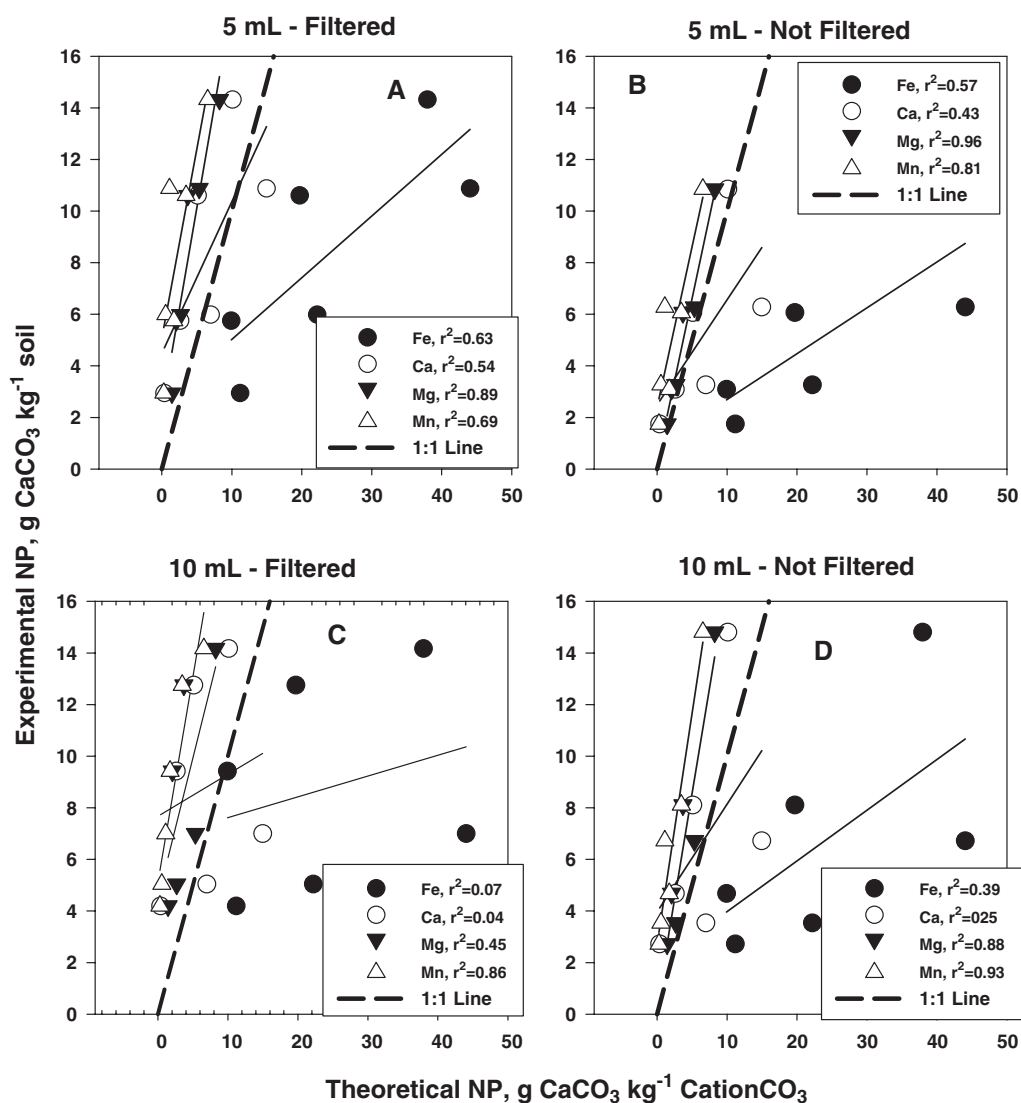


Fig. 6. Experimental neutralization potential (NP) values of H₂O₂ treatments as compared to theoretical values obtained using stoichiometric relationships describing the dissolution of Fe, Ca, Mg, and Mn carbonates under acidic testing conditions.

MnCO₃ dissolution than NP values obtained using the filtered treatments. The NP values obtained from the 5 mL treatments were more strongly correlated to theoretical NP values based on oxidation and hydrolysis of Fe than the 10-mL treatments. The data indicate that in the presence of an excess of oxidant, the theoretical equation for the dissolution, oxidation, and hydrolysis may not be as accurate as in the presence of a lesser amount of H₂O₂.

Precipitates with pale yellow to dark red colors were formed after the addition of H₂O₂ to samples. The exact colors varied with siderite concentration and were indicative of formation of Fe hydroxides or intermediate oxidation products. Samples containing 2.5% siderite were pale yellow (5Y 8/4) and those containing 5.0% siderite were yellow (10YR 7/8). Samples with 10.0% siderite were dark red (2.5YR 3/6) after the addition of H₂O₂ and heating for 5 min. Precipitate colors after titration with NaOH were red (2.5YR 5/8) to dark reddish brown (2.5YR 3/4), suggesting that Fe²⁺ was oxidized to Fe³⁺ and hydrolyzed to ferrihydrite or lepidocrocite (γ-FeOOH). X-ray diffraction analysis of precipitates formed after NP determination of the siderite samples with H₂O₂ showed peaks characteristic of 2-line ferrihydrite (Fig. 7). The poorly ordered 2-line ferrihydrite results from rapid hydrolysis of Fe³⁺ at pH > 5 and its chemical formula is not known, although several formulas have been suggested (Schwertmann et al., 1995). X-ray diffraction peaks for feroxyhyte (δ-FeOOH) are similar with those for 2-line ferrihydrite, therefore both Fe-oxides may be present. Oxidative hydrolysis of Fe(II) salts with rapid oxidation using H₂O₂ can produce δ-FeOOH (Schwertmann and Cornell, 1991).

These data indicate that the precipitates produced when FeCO₃ is oxidized with H₂O₂ are not representative of field weathering of siderite, which commonly produces goethite.

Potassium Permanganate

Data in Fig. 3C show that 80% of the variability in NP when determined with KMnO₄ is due to CO₃²⁻ concentration. Experimental NP values were highly correlated with Mg ($r^2 = 0.93$) and Fe ($r^2 = 0.74$) concentration in the siderite sample. Manganese concentration of the siderite sample was also correlated with NP values after oxidation. Decreases in NP were directly related to Fe concentration ($r^2 = 0.60$). Neutralization potential values decreased after oxidation with KMnO₄; however, the values were higher than NP values obtained when treated with H₂O₂ or O₂ (Fig. 4). Higher NP values after the KMnO₄ treatment versus other oxidation treatments may be due to only partial Fe²⁺ oxidation as a result of the weaker oxidizing power of KMnO₄ under NP testing conditions.

Oxidation with KMnO₄ decreased NP values of reagent-grade FeCO₃ slightly (Fig. 2). Data in Fig. 2 show that CaCO₃ and MnCO₃ NP values were not significantly affected by oxidation.

Due to the deep purple color resulting from the reaction of KMnO₄ with the precipitates formed during titration, precipitate colors were not analyzed after oxidation and titration. X-ray diffraction patterns show the formation of 2-line ferrihydrite after treatment with KMnO₄. The XRD data also suggests the presence of noncrystalline or poorly ordered Fe-hydroxides (Fig. 7).

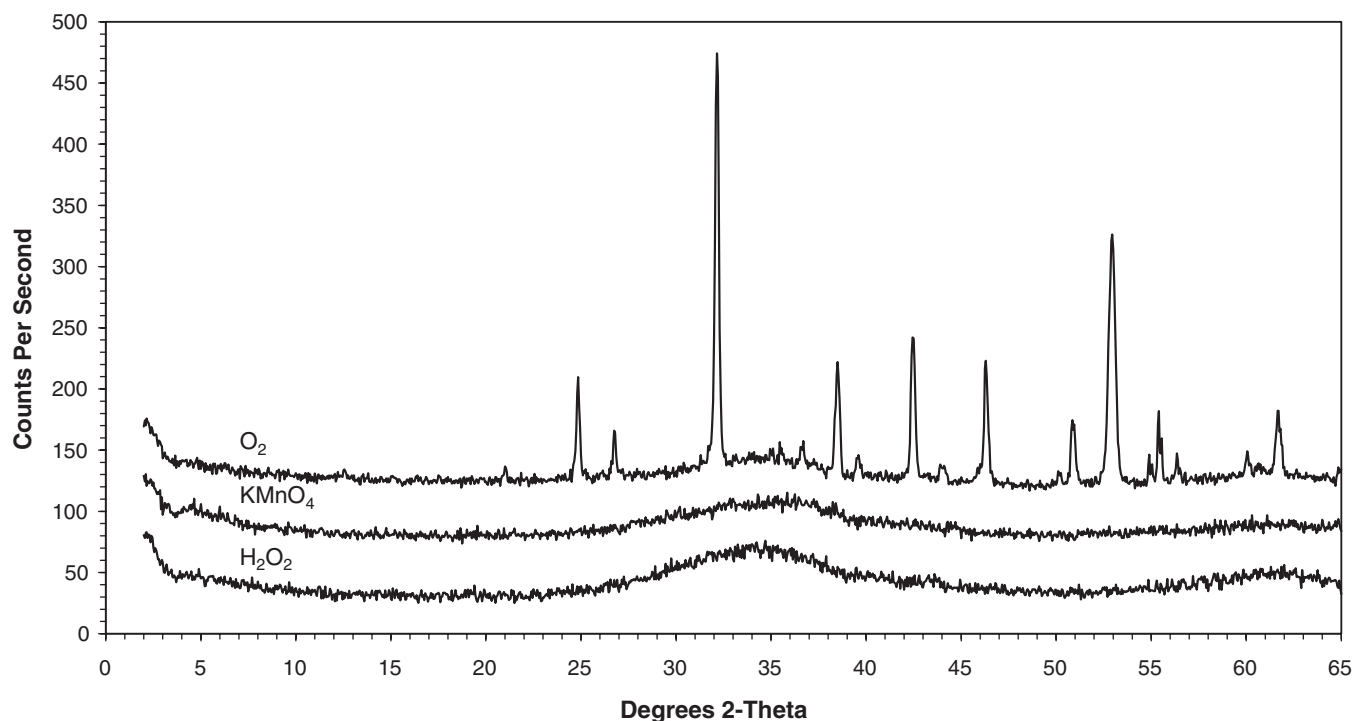


Fig. 7. X-ray diffraction patterns for the dissolution products formed from siderite using O₂, KMnO₄, and H₂O₂. The sharp peaks on the O₂ pattern correspond to residual siderite.

Hydrolysis of acidic solutions of Fe(III) salts can produce hematite, akaganeite, goethite, and ferrihydrite. Which product forms and its degree of crystallinity is dependent on temperature of reaction, pH, rate of hydrolysis, and the nature of the anions present. Unless the reaction conditions are controlled precisely, a mixture of products will form (Schwertmann and Cornell, 1991). The reaction products of KMnO_4 and FeCO_3 are poorly ordered and therefore not representative of atmospheric oxidation of FeCO_3 .

Oxygen

After oxidation with O_2 , NP values are no longer relative to Fe concentration, suggesting that FeCO_3 was oxidized and hydrolyzed during testing, eliminating the FeCO_3 interference (Fig. 3D). Remaining NP values were dependent on Mg and Mn concentration. Data in Fig. 4 show that NP values significantly decreased after samples were oxidized with O_2 . Neutralization potential values were not significantly different between the H_2O_2 and O_2 treatments for all samples containing <0.2 g (10%) of sample. The NP values obtained after the O_2 treatment were lower than values from the H_2O_2 treatment for samples containing 10% siderite indicating that there may not have been enough oxidant for oxidation and hydrolysis of all the Fe in the sample. The decrease in NP values after oxidation is highly correlated with Fe present in the sample ($r^2 = 0.99$).

The NP values of reagent-grade FeCO_3 decreased after oxidation with O_2 as compared with NP values obtained after oxidation with H_2O_2 (Fig. 2), indicating that O_2 had a greater oxidizing effect on the Fe present in the sample than H_2O_2 . The NP values of reagent-grade MnCO_3 were less after treatment with H_2O_2 as compared with NP values obtained after treatment with O_2 . Data in Fig. 2 show that CaCO_3 NP values were not significantly affected by oxidation with O_2 .

During NP testing, green precipitate forms on the initial addition of NaOH, which is converted to a red precipitate on exposure to O_2 indicating the Fe^{2+} in solution is oxidized. Titration with NaOH should proceed slowly so that O_2 has ample time to oxidize Fe^{2+} in the sample and to avoid missing the endpoint at pH 7.0. The color of precipitates formed after complete oxidation with O_2 and titration with NaOH were dark reddish brown (2.5YR 3/4), suggesting that Fe^{2+} was oxidized to Fe^{3+} and hydrolyzed to ferrihydrite, lepidocrocite ($\gamma\text{-FeOOH}$), or an amorphous Fe oxide during testing. The transformation of FeCO_3 to $\gamma\text{-FeOOH}$ or $\alpha\text{-FeOOH}$ after oxidation with O_2 is consistent with atmospheric weathering of FeCO_3 under natural conditions (Senkayi et al., 1986; Frisbee and Hossner, 1995).

The XRD pattern of precipitates formed after oxidation with O_2 and subsequent titration to pH 7.0 suggests the formation of Fe oxides with a poorly crystalline structure or the formation of mixed reaction products (Fig. 7). Peaks at approximately $32^\circ 2\theta$ and $52^\circ 2\theta$ denote siderite, which was not completely dissolved in 0.1 M HCl. Incomplete dissolution of siderite is not a problem since dissolution of FeCO_3 and oxidation and hydrolysis

of Fe^{2+} should produce a neutral reaction under natural weathering conditions. Neutralization potential analysis conditions, when using O_2 as an oxidant, are similar to laboratory conditions for the synthesis of $\gamma\text{-FeOOH}$ (Schwertmann and Cornell, 1991). Oxidation and hydrolysis of Fe(II) salts produces lepidocrocite, goethite, magnetite, and ferrihydrite. Goethite and $\gamma\text{-FeOOH}$ form at pH values between 6 and 7. With rapid oxidation, using H_2O_2 , feroxyhyte ($\delta\text{-FeOOH}$) is produced (Schwertmann and Cornell, 1991). Laboratory synthesis of $\gamma\text{-FeOOH}$ involves dissolving FeCl_2 salt in water, adjusting the pH to 6.7 to 6.9 with NaOH, then adding an air supply to bubble through the solution. The initial gray color formed changes to orange with time. The entire process takes 1 to 3 h. The degree of crystallinity of minerals formed depends on reaction conditions. Mixtures of minerals form, rather than a single product, unless reaction conditions are carefully controlled. Reaction pH must remain constant to obtain a crystalline product. During NP testing, the pH is steadily increased with NaOH and O_2 is bubbled through the solution throughout titration. In contrast to the laboratory conditions for the synthesis of $\gamma\text{-FeOOH}$, the titration used in NP determinations is completed in <1 h and this is insufficient time to allow crystalline phases to form.

CONCLUSIONS

Neutralization potential values of samples containing siderite were the highest when USEPA Method 600/2-78-054 3.2.3 was used. Oxidation and hydrolysis of Fe with H_2O_2 , KMnO_4 , O_2 lowered NP values compared with USEPA Method 600/2-78-054 3.2.3. Oxidation with H_2O_2 (5 mL, filtered) and O_2 produced similar NP values and were not highly correlated with Fe concentration (based on the correlation of determination values). The O_2 method was relatively faster to perform and might be preferred in an analytical laboratory setting. Neutralization potential values were reduced after oxidation with KMnO_4 ; however, they were still highly correlated with Fe concentration.

The authors agree that the preferred method for NP determination for samples containing siderite is as follows:

1. Weigh 2 g of a soil sample that has been processed and sieved to <60 mesh (250 μm) into a 200-mL beaker.
2. Add 20 mL of 0.1 M HCl and heat on a hot plate at 121°C for 15 min or until reaction appears to be complete (sample will settle on the bottom of the flask at this point).
3. Add distilled water to a volume of roughly 125 mL into the beaker and cover with a watch glass.
4. Boil the contents of the beaker for 1 min.
5. After the samples have boiled for 1 min, turn the hot plate off and remove the samples from the hot plate to cool.
6. Remove the watch glass and rinse the liquid on watch glass into the beakers with the samples.

Analysis should not continue until the samples have returned to room temperature.

7. After the samples have cooled to room temperature, place the 200-mL beaker containing the sample on the stir plate and equip with stir bar.
8. Begin stirring sample while adding NaOH to the burette. Take a calibrated reading of the burette.
9. Rinse pH probe on a calibrated meter with de-ionized water in a separate cup, then place the probe in the sample.
10. Note the pH of the sample before beginning titration.
 - a. If the pH is greater than 6.0, the sample must be reweighed and digested using 40 mL of HCl.
 - b. If the pH is approximately 2.0 to 3.0, the sample is ready to be titrated.
11. Equip the flask containing the digested sample with a small fish-tank aerator attached to a tank of O₂ and turn on tank slowly so as to gently bubble O₂ through the sample.
12. Begin to slowly titrate the sample with NaOH while it is being aerated and stirred. Bubble O₂ through the sample for the duration of the titration. The length of time that the solution is in contact with the O₂ will vary depending on the amount of acidity consumed during digestion (i.e., the amount of time needed to neutralize remaining acidity with NaOH).
13. When the sample maintains a pH between 6.95 and 7.05 for 30 s, take a reading of the burette and record the result.

Neutralization potential is calculated using Eq. [17]:

$$(\text{mL HCl} \times M \text{ HCl}) - (\text{mL NaOH} \times M \text{ NaOH}) \times 25 \\ = \text{tonnes CaCO}_3 / 1000 \text{ tonnes material} \quad [17]$$

After all oxidation treatments, NP values were highly correlated with Mn content. This is of concern since hydroxyl ions may be consumed during the oxidation and hydrolysis of Mn released during weathering of Mn carbonates, which will not result in the consumption of acidity (Dixon et al., 1982). Therefore, false positive NP values may result when MnCO₃ or other carbonates substituted with Mn are present in overburden. Further investigation on the effects of acid digestion and oxi-

dation of Mn, as well as other minerals, during NP testing is warranted.

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